

## Role of fluorine ions in the formation of silica gel structure and gel glass<sup>\*</sup>

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Fluorine containing silica gels can be used as precursors of anhydrous glasses for fibre optics. The silica gels were prepared by the sol-gel process including the following stages: hydrolysis of tetraethylorthosilicate (TEOS) in a four-component system  $\text{Si}(\text{OC}_2\text{H}_5)_4\text{--C}_2\text{H}_5\text{OH--H}_2\text{O--HCl}$ , addition of fumed silica (aerosil) into the sol, sono-activation, centrifugal separation, neutralization by the ammonia solution, gelation, washing the gels in distilled water, drying and fluorination of the xerogels by the procedure of heating in the freon/oxygen atmosphere or impregnation in F-containing solutions. Fluorinated gels were consolidated into transparent silica glass in the atmospheres of air or helium gas at temperatures of 1200–1300 °C. SEM and AFM analysis and BET surface area investigations were used for characterization of the xerogels and glasses morphology. The optical properties of pure and fluorine-containing silica glasses were studied by VIS- and IR-spectroscopes.

### 1. Introduction

Fluorine has recently become a popular dopant for lowering of the refractive index of pure silica glasses for optical fibres [1]. Also, the F-doped, graded-index (GI) fibres with low OH content may be proper candidates for operation at 0.85 and 1.3  $\mu\text{m}$ , since they display basically low losses at 1.3  $\mu\text{m}$ , what differs them from other fibres-including boron oxide [2]. Utilization of the sol-gel process for synthesis of fluorine-doped silica glass is preferable because of its low sintering temperature and high efficiency [3]. Incorporation of fluorine into a xerogel reduces bubble formation upon consolidation by sintering and eliminates glass bloating during fibre drawing at high temperatures (2000–2200 °C). The fluorine doping is a very complicated process [3]. As shown for the gas phase doping, F content depends on the specific surface area of the starting dry gels and the conditions of the treatment. The defluorination by liberation of  $\text{SiF}_4$  at high temperatures results in lowering of the dopant content in silica glasses and forming of the refractive index gradient in silica-glass rod-like pre-forms. The method of the liquid-phase doping by addition of the fluorinated silicon alkoxide ( $\text{Si}(\text{OC}_2\text{H}_5)_3\text{F}$ ) into the sol solutions results in rising of the F content in the silica glasses [1].

The method of the liquid-phase doping by using F-containing compounds ( $\text{NH}_4\text{F}$ ) was previously described [4]. However, maximum values of the fluorine contents were limited

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to 0.2% (by weight). The mechanism of the F-doping into gel pre-forms by using  $\text{NH}_4\text{F}$  as a fluorine source and structural behaviour of the dopant ions in the silica gels and glasses has been also described [5]. Silica xerogels made by a modified sol-gel process were used for the liquid phase F-doping with organic solutions of  $\text{NH}_4\text{F}$  and  $\text{HF}$  [6].

This paper describes the fabrication technique yielding fluorine-doped silica gels and glasses in the modified sol-gel process and the effect of F ions on structural properties and morphology of the xerogels. Optical properties of sintered pure and fluorinated silica glasses are also discussed.

## 2. Experimental

The F-doped xerogels and glasses were prepared by the sol-gel process [6] with the doping technique. The flowchart of the modified sol-gel process is shown in Fig. 1 and it displays the following stages: the TEOS hydrolysis in the system  $\text{Si}(\text{OC}_2\text{H}_5)_4\text{--C}_2\text{H}_5\text{OH--H}_2\text{O--HCl}$  with mole ratio 1:2:16:0.01 by vigorous mixing in fluoroplastic reactor in the air, addition of fumed silica with a specific surface  $200\text{ cm}^2/\text{g}$  (aerosil T30, Wacker-Chemie GmbH, Germany) into the sol as a tiller, ultrasonic dispersion with vigorous stirring and centrifugal separation from agglomerates and dust particles. Then, the sol-colloidal system was neutralized (up to  $\text{pH} = 6.5$ ) with the help of an ammonia solution and cast into fluoroplastic moulds to yield solid gels shaped as disks and rods. The wet gels were formed during 20–30 min in sealed containers; then the containers were opened and the gels were washed with distilled water.

The resulting gels were dried slowly at 30–60 °C for 7–14 days in the air. The drying step should not induce cracking or warping of large gels. This was ensured by employing special containers: thorough and unidimensional removal of solvents and water was provided (no mechanical stresses were accumulated). After drying the xerogels were doped with fluorine by the gas-phase or liquid-phase dopings. The mixture of freon ( $\text{C}_2\text{Cl}_3\text{F}_3$ )/oxygen was used for the gas-phase doping. Dried xerogels were placed in pure silica glass tubes in a horizontal furnace and the temperature was increased up to 1000 °C with the rate of 250°/h. The mixture of freon/oxygen gases was flowed into the tube at room temperature with the rate of  $0.2\text{ dm}^3/\text{min}$ . During heating in oxygen the organic compounds were burned out at about 500 °C and fluorine was incorporated

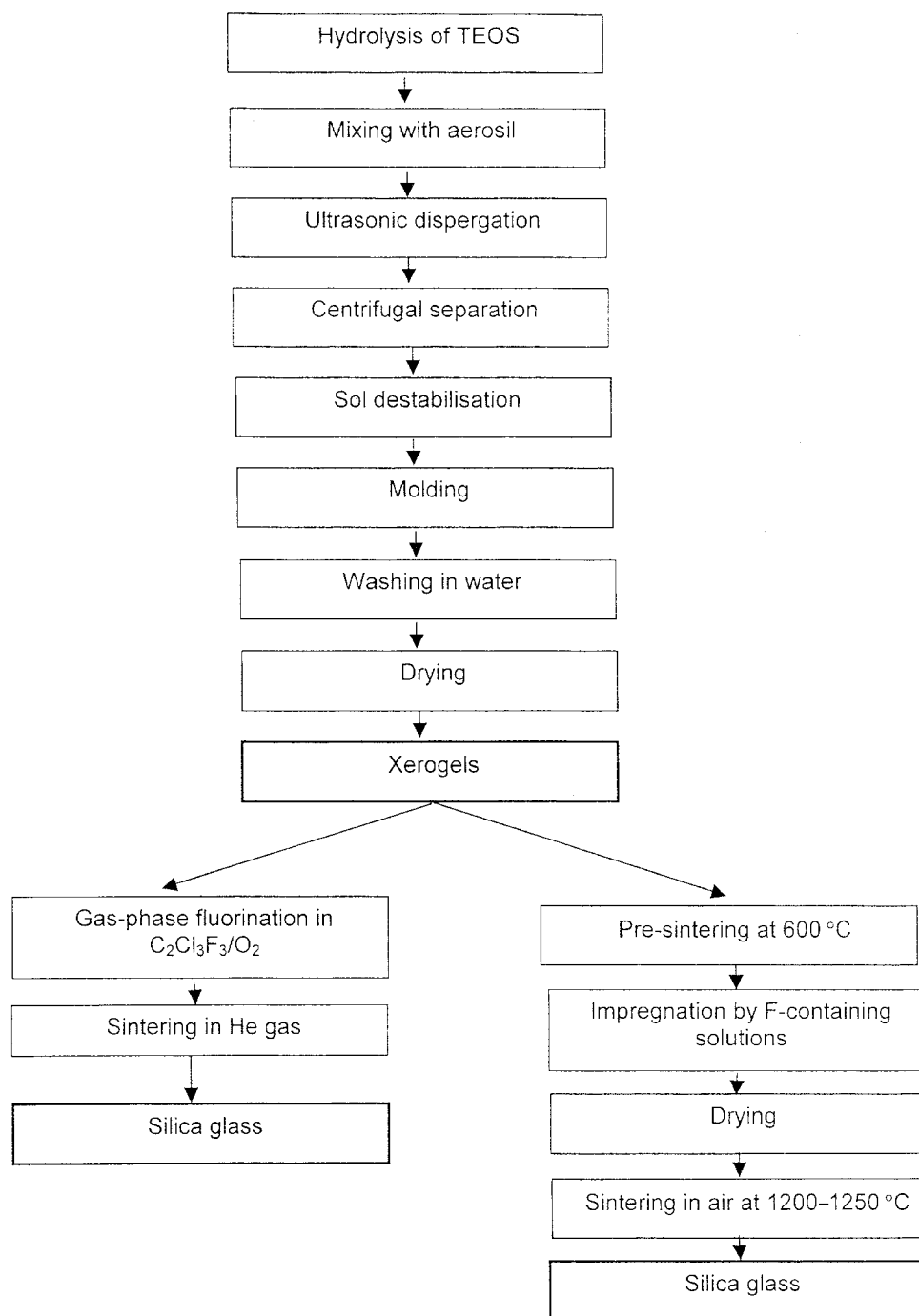


Fig. 1. Scheme of the silica gel glass preparation

into the porous gel structure, replacing the OH groups. The modified liquid-phase doping procedure does not require high temperatures for the fluorination and the process of introducing OF the F ions into xerogels takes place at the room temperature. The pre-sintered xerogels (600 °C, in the air) were impregnated in organic solutions containing the F ions. Such organic solvents as acetone, ethanol and isopropanol were employed due to their low surface tension.

F-containing water solutions used for the gels impregnation resulted in cracking the monolithic gels into fragments. The impregnation of the disk samples in the F-containing solutions was performed in vacuum (5–10 Torr). The modified gels were dried at 30–60 °C for 10–14 h. The consolidation into the transparent silica glasses was carried out at 1200–1300 °C in the air atmosphere. Using F-containing organic solutions for the doping allows us to obtain transparent silica glasses without cracks or warping. The specific surface areas and related pore volumes of the drying gels (xerogels) were measured by the BET method using argon adsorption at the liquid nitrogen temperature. The pore size distribution was calculated from the benzol adsorption-desorption isotherms [7].

Samples of the xerogels dried at 60 °C have been heated in the air from room temperature up to several final temperatures varying from 60 °C to 1200 °C (60 °C; 600 °C; 800 °C; 1000 °C; 1100 °C; 1200 °C). The samples were exposed for 2 h to each temperature.

The SEM and AFM analyses were used for characterization of the xerogels and sintered glasses morphology during the course of the samples heating. Optical absorption spectra were measured using the glass samples 2–4 mm thick by means of a spectrophotometer SPECORD IR-75 (in the IR-region) and BECKMAN-5270 in the visible and UV-regions.

The hydroxyl content in dense glass samples has been calculated from the IR absorption spectra using the relationship [8]:

$$[\text{OH}] \text{ [ppm]} = \frac{1000}{t} \log \frac{T_a}{T_b}$$

where:  $t$  – sample thickness (mm),  $T_a$  – transmission at 2.6  $\mu\text{m}$ ,  $T_b$  – transmission at 2.72  $\mu\text{m}$ .

The refractive index ( $RI$ ) of the fluorinated glass was measured using spatial filtering technique employing pure silica glasses as a standard. The RI-profiles in rods, prepared by the method of gas-phase doping, were measured using special equipment (P102 York Technology Ltd.). The effective fluorine and chlorine concentrations in silica gel glass were measured by the method of micro-X-ray diffraction spectral analysis (MXRSA) (CAMEBAX, France).

### 3. Results and discussion

#### 3.1. Porosity and morphology of gels

The porosity parameters and specific surface area ( $S$ ) for the xerogel and glass samples heated at a temperature range 60–1200 °C in air are given in the table.

Table. Porosity parameters and specific surface area ( $S$ ) for the xerogel and glass samples

Sample	Temperature of treatment/°C	$S/(\text{m}^2/\text{g})$	Pore volume/ $(\text{cm}^3/\text{g})$	Maximum $d_{\text{pore}}/\text{nm}$	Remarks
1	60	226	0.528	2.5, 13.0	bimodal trimodal
2	600	224	0.718	2.5, 6.0, 12.0	
2F*	600	197	0.254	3.0, 5.0, 25.0	
3	800	250	0.825	2.5, 6.0, 20.0	
4	1000	233	0.605	3.0, 6.0, 23.0	
5	1100	6.2	0.013	3.0, 5.0, 23.0	silica glass
6	1200	0.0	0.0	nonporous	

\*The sample fluorinated at 600 °C by the liquid-phase doping technique.

From the consideration of the table we can state that pore volume increases until heating up to 800 °C and when the temperature rises up to 1100 °C the process of pore collapse is began, resulting in 1.6% of porosity. At the temperature of 1200 °C the pores are eliminated and the density becomes equivalent to fused silica.

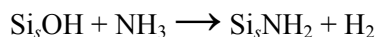
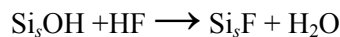
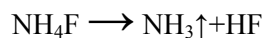
There is a little change in the pore distribution of the hybrid silica gels until heating to the interval 800–1100 °C. Densification primarily is due to only the number of pore decreasing.

During heating of xerogels up to 600 °C the densification process of silicate skeleton takes place, the liquid is removed from the interconnected pore network, the organics are burned and  $\text{NH}_4\text{Cl}$  is sublimated. The pore volume increases as a result of the surface area and pore size rising.

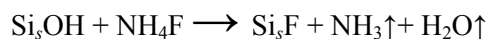
Polycondensation reactions continue to occur within the xerogel network and removing of intermicellous liquids increases the surface area (up to 800 °C). Then the removal of hydrogen-bonded water ( $\text{Si}-\text{OH}\cdots\text{H}_2\text{O}$ ) and surface silanol ( $\text{Si}_s-\text{OH}$ ) groups (partially) from the pore network results in chemically stable and mechanically durable xerogels [9].

The pore distribution for undoped (1) and liquid-phase fluorinated (2) silica xerogels fired at 600 °C are shown in Fig. 2. It is seen that soaking of silica xerogels in the solution of F-containing chemicals ( $\text{NH}_4\text{F}$  + acetone) followed by heating at 600 °C in air, results in the loss of specific surface area and increasing of a pore size. The pore-size distribution of fluorinated gels also has a trimodal character: the network contains micropores (3.0 nm), mezo- and macropores (5.0–25.0 nm). The pore size

can be large by chemical attack of silica network with fluorine ions in solution and also in vapour phase until heating and dissociation of ammonium fluoride [10]:



or directly:



The fluorinated gels have been densified in air in the temperature as low as 1150–1180 °C.

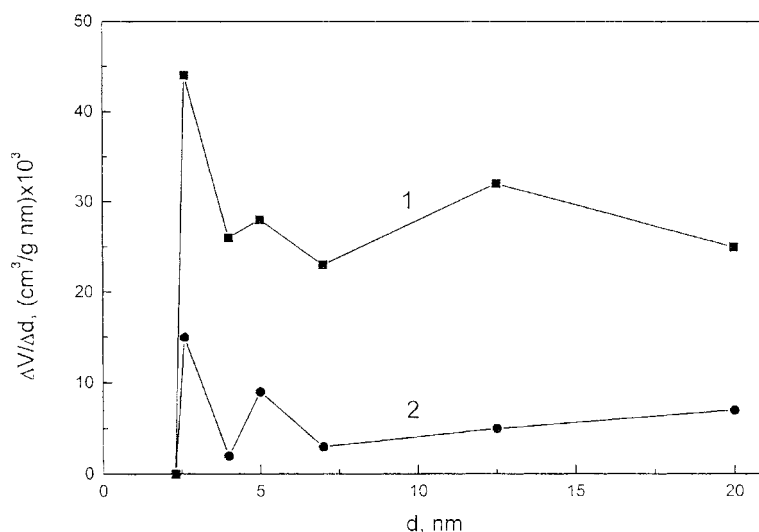


Fig. 2. Pore size distributions in undoped (1) and fluorinated (2) silica xerogels fired at 600 °C

Figure 3 shows SEM fracture surfaces of xerogel samples, heated at 60 °C (A); 600 °C (B) and 100 °C. The photos A and B display that the xerogel structure is formed from globular-chain units. The pore network contains the pores of transition character. The structure of sample 5 (the table) has a globular topology with a small volume of macropores (pre-glass). The authors [11] suggest that the formation the layered structure in hybrid gels may be possible and results from the polymerization of alkoxide-derived fractal particles in hybrid sol-gel systems.

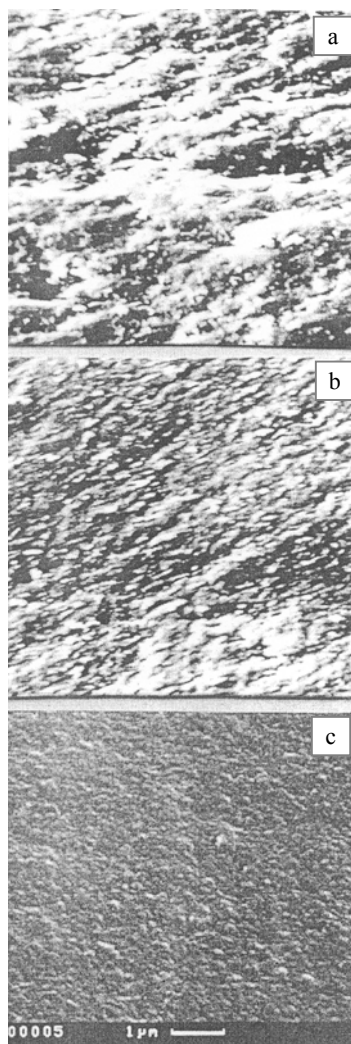


Fig. 3. SEM photos showing the fracture surfaces of xerogels heated at 60 °C (a), 600 °C (b) and 1100 °C (c)

Sample 6 (sintered silica gel glass) after chemical etching in 40% HF (Fig. 4) shows the globular structure, formed from units having the dimensions of about 100 nm probably from the reorganization of globular-chain agglomerates.

The Atomic Force Microscopy (AFM) analysis at 600 °C-heated samples shows that the structure of fired xerogels has a rigid character with the units dimensions of about 10–20 nm and corresponds with SEM morphology.

The fracture surface of the fluorinated silica gel glass, sintered in helium gas after the process of vapour-phase doping (from the mixture freon/oxygen) has been observed using an AFM microscope. A homogeneous structure formed from units sized of about 5–10 nm can be seen. The roughness and the globule dimensions of fluorinated gel-glass structure are decreased and the transparency of F-containing glass rises, compared with the undoped gel glass.

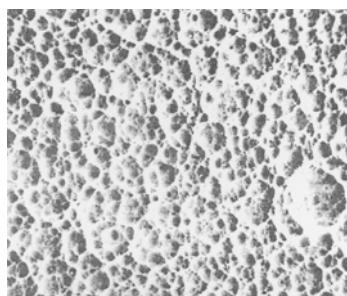


Fig. 4. SEM photo of etching surface of silica gel glass (40% HF, 30 min), magnitude  $\times 500$

### 3.2. Optical characteristics of undoped and fluorinated silica gel glasses

A major problem in producing silica gel-glass optics is removal of surface hydroxyl groups and hydrogen-bonded pore water, which gives rise to atomic vibration energy absorption in almost the entire range from ultraviolet to infrared radiation (160–4500 nm) and decreases the optical applications of silica gel monoliths [9].

Some fluorine-containing compounds (HF,  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{HF}_2$ ,  $\text{CF}_2\text{C}_2$ ,  $\text{C}_2\text{F}_3\text{Cl}_3$  etc.) can react with surface hydroxyl groups and gel silica network at elevated temperature, replacing OH ions and forming the fluorine-containing volatile substances ( $\text{SiF}_4$ ,  $\text{SiF}_3$ ).

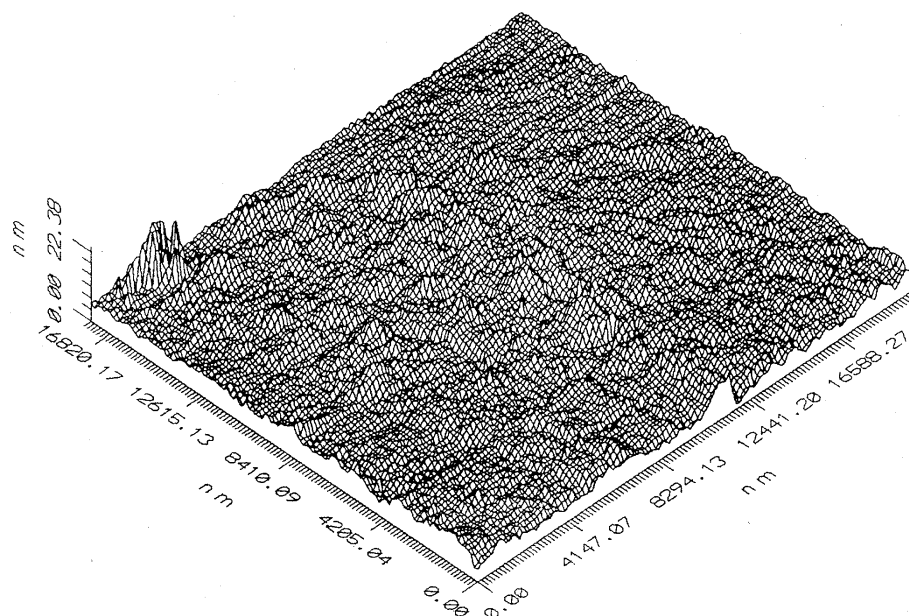


Fig. 5. AFM topography of silica gel (600 °C) fracture surface

The IR spectrum of gel glass samples is shown in Fig. 7. The sample thickness was  $4.0 \pm 0.1$  mm. The undoped silica gel glass, prepared by the vitrification at the temperature of 1200 °C in air without any special dehydroxylation contains the hydroxyls between 2000 to 2500 ppm (curve 1).

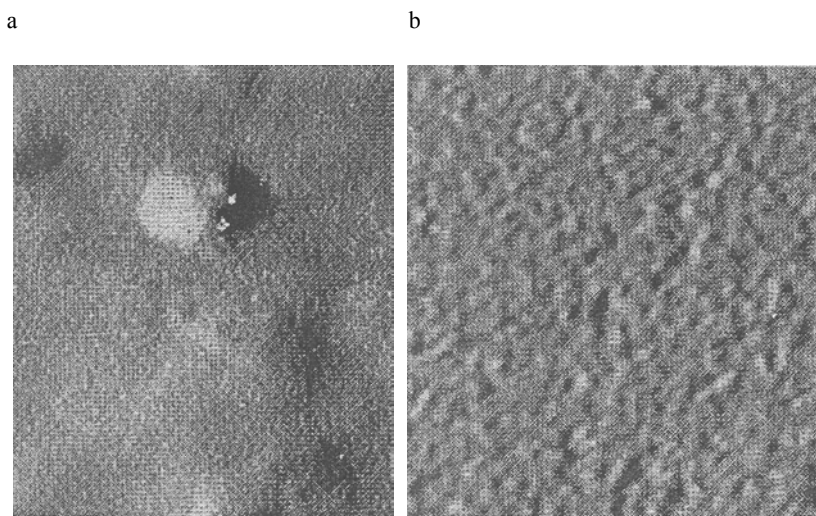


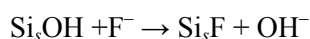
Fig. 6. AFM micrographs of fluorinated silica gel glass.  
Scale images: a)  $10 \times 10$   $\mu\text{m}$ , b)  $1.7 \times 1.7$   $\mu\text{m}$



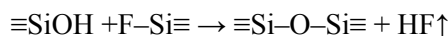
By liquid-phase doping procedure it is probably not possible to eliminate completely the OH groups from the silica porous network surface and a significant part of hydroxyl ions remains in the volume of glass after consolidation. The  $k_\lambda$  for samples 2 and 3 (Fig. 7) corresponds to the residual OH<sup>-</sup> content of 30–80 ppm.

The process of gas-phase fluorine doping reduces hydroxyl level in the dense silica glass to below 3–5 ppm (curve 4 in Fig. 7). The contents of fluorine determined by the MXRSA for sample 4 is 0.4–0.45% by weight. Such glasses have about 90% transmission at 3671 cm<sup>-1</sup> (hydroxyl group absorption) region. The gas-phase doped sample contains also the chlorine contamination of 0.17% by weight.

At the temperature higher than 600 °C the F-containing compounds (obtained in the process of thermo-destruction of freon/oxygen mixture) attack the gel network and the reaction of OH<sup>-</sup> groups substitution takes place:



During the densification process in the He gas atmosphere (1000–1300 °C) both hydroxyl and fluorine ions remain in the adjacent sites on the surface of the pore structure and the condensation reaction takes place with the elimination of HF [5]:



The F-containing substances volatilized during the process of xerogel consolidation in helium gas can result in forcing the gradient of refractive index in glass body.

The refractive index of the sintered in air silica glass measured  $n_D^{\text{air}} = 1.4570$  and was decreased by sintering in helium gas after the fluorination in freon/oxygen atmosphere ( $n_D^{\text{F}} = 1.4532$ ). A special technique of double gas fluorination was employed for the preparation of silica glass with minimum refraction index value  $n_D^{2\text{F}} = 1.4507$  and the hydroxyl level to below 1 ppm.

By the method of gas-phase fluorination the rod pre-forms for optical fibre drawing were prepared. Typical size of the glass rods was 22 mm in diameter and 130 mm long. A pre-form has a gradient refractive index profile owing to fluorine removing from the external layers of porous rod during the consolidation process in helium. The refractive index difference  $\Delta n$  between external and internal parts of pre-form equals 0.00042.

## 4. Conclusions

Silica glasses doped with fluorine were prepared by the sol-gel method using gas-phase and liquid-phase doping.

The process of gas-phase fluorination with using of freon/oxygen mixture results in preparing of silica gel glass with the concentration of OH<sup>-</sup> groups of 1–5 ppm. Liquid-phase doping procedure is probably not able to eliminate the hydroxyls completely and the residual OH content is 30–80 ppm.

The study of morphology and porosity parameters by the SEM, AFM and BET methods has shown the effect of fluorine ions on pore structure and specific surface area of xerogels. Fluorinated gels are of low pore volume and decreased specific surface area. Effective fluorine concentrations are between 0.2 and 0.45% by weight.

The refractive index  $n_D$  of the air-sintered silica gel glass is 1.4570 and for the fluorinated samples it decreased to  $n_D^{2F} = 1.4507$ .

By the method of gas-phase fluorination the rod pre-forms for optical fibre drawing were prepared with typical size of 22 mm in diameter and 130 mm long. A pre-form has a gradient refractive index profile because of partially fluorine removing and the difference consists  $\Delta n = 0.00042$ .

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